#### TITLE OF THE INVENTION

O1 Accelerating the Coloring of Concrete and Other Substrates

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of United States provisional application no. \* filed January 24, 2002.

# BACKGROUND OF THE INVENTION

- The coloring of concrete and other substrates with metal compounds, some of which are commonly described as acid stains, is a relatively new industry that is expanding rapidly. The technique provides visually appealing colors to a normally dull surface. Acid stains have a range of colors which depend on the metal compounds used. Under skillful application, the substrate may be made to look like granite, marble or other high quality construction material.
- Under prior art, the staining process relies upon natural development of the color under atmospheric conditions, usually in the presence of water. Atmospheric conditions for a reaction means that the reaction takes place exposed to the earth's atmosphere, although it will be appreciated that this atmosphere may be altered slightly by contaminants from local conditions, such as vapors from building or cleaning materials. The process of color development can be very slow, taking hours or even days to complete. Costs are increased since applicators may have to visit application sites several times. Furthermore, the end of the color development, and thereby the final color of the stain, is difficult to predict. Some stains contain chromates (chromium(VI)-compounds), such as sodium dichromate, which somewhat accelerate color development in select colors. Chromates are, however, strongly suspected to be carcinogenic and are only useful in darker colors.

Industry literature generally states that concrete exhibits varying degrees of alkalinity on its surface. It is said that regions of lower alkalinity treated with metal compounds develop color much slower or not at all. The industry currently sells sodium hydroxide and sodium bicarbonate to applicators to improve staining of difficult-to-stain substrates. Even after treating concrete with these alkali, reactions are still generally slow, and it may take hours or days for colors to fully develop.

## SUMMARY OF THE INVENTION

- The present invention overcomes these shortfalls, permitting light and dark colors of a stained substrate to be developed within less than 15 minutes. According to an aspect of the invention, an oxidizer is applied to a stained substrate and allowed to react. After the colors are developed, excessive metal compounds and oxidizer may be rinsed off. The decoratively stained substrate may be protected and finished according to conventional practices.
- Therefore, according to an aspect of the invention, there is provided a method of treating a substrate that contains an oxidizable metal compound, the method comprising the step of contacting the substrate with an oxidizer to increase the development speed of the color of the oxidizable metal compound. The application of the oxidizer may also be used to develop a specific color. The substrate may be natural, or manmade, such as a hydraulic material, for example concrete. The oxidizer is preferably free of chromates as they are suspected to be carcinogenic. The oxidizer is preferably applied to the substrate in liquid solution, such as in aqueous solution, and may be applied with an acid or base in aqueous solution to ensure oxidative conditions. The oxidizer may for example be selected from the group consisting of peroxides, percarbonates, perborates, peracetates, permanganates, chlorates, perchlorates, peroxymonosulfates, peroxo disulfates,

bismuthates, peracids, and organic peroxo compounds, and may be present in solution in an amount from 0.1% to 100% by weight. Any of various construction materials and other substrates may be treated in this manner.

These and other aspects of the invention are described in the detailed description of the invention and claimed in the claims that follow.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

- In this patent document, "comprising" means "including" and does not exclude other elements being present. In addition, a reference to an element by the indefinite article "a" does not exclude the possibility that more than one of the elements is present.
- A substrate is any material having a surface that in use is exposed to viewing and that may be stained with a metal compound. Example of substrates are floors, walls, decks, playground surfaces, driveways, sidewalks, roadways, paths, paving stones, tiles, roofing tiles, and architectural features such as countertops, tables, columns, facades and statues. Substrates include man-made materials, for example blocks, bricks, concrete, polymer modified concrete, including overlays, cementitious materials, or other hydraulic materials, and natural materials, for example limestone, marble, and slate. A hydraulic substrate is a substrate made with inorganic compounds that cure by reaction with water.
- A metal compound means a chemical compound containing metal cations that are oxidizable and have a desirable color in their higher oxidational state. Examples include metal salts or complexes, mixed metal salts and/or complexes, or mixtures of metal salts and/or complexes. The metal compounds contain cations of metals of the IIIa Group to Va Group, and/or the Ib Group to VIIIb Group elements. Preferred oxidizable metal

compounds contain cations of titanium, vanadium, chromium, molybdenum, manganese, iron, cobalt, nickel, copper, zinc, cadmium, tin, and bismuth.

- Other than with the oxidizers described in the present invention, metal compounds may react with chemical components of the substrate, atmosphere, and simultaneously or sequentially added reagents (other than oxidizers), to form a mixture of reaction products. These chemical components include, but are not limited to, water, oxygen, carbon dioxide, hydroxides, phosphates, and calcium ions. Some metal compounds may, for instance, oxidize naturally under atmospheric conditions and slowly form colored compounds that permanently stain the substrate and give it an aesthetic, natural, or weathered appearance. An example of such a reaction is cited below.
- An oxidizer is a substance having a sufficient redox potential to oxidize metal cations or mixtures of metal cations in salts or complexes from a lower oxidational state to a higher oxidational state faster and preferably significantly faster than the naturally occurring process by oxidation with atmospheric oxygen, where the metal cations in the higher oxidational state show a desirable color, and are capable of permanently staining a natural or man-made substrate, and give it an aesthetic, natural, or weathered appearance.
- Oxidizers include, but are not limited to, peroxides, percarbonates, perborates, peracetates, permanganates, chlorates, perchlorates, peroxymonosulfates, peroxo disulfates, bismuthates, derivatives of peroxo acids (peracids), and organic peroxo compounds. Preferred oxidizers include peroxides, percarbonates, perborates, peroxymonosulfates, and peroxo disulfates. Combinations of oxidizers may be used, such as a combination of hydrogen peroxide and sodium percarbonate. A particularly strong oxidizer is sodium peroxide.

As well known to those skilled in the art, the redox potential is generally dependent on the concentration of all reagents participating in the redox reaction, and may, therefore, also be dependent on the pH. For the reactions described in this invention, the pH is determined by the chemical composition of the substrate, the type and concentration of the metal compounds to be oxidized, and the type and concentration of the oxidizers. The pH may have to be altered in consideration of the chemical composition of the substrate (since a substrate may show undesirable reactions at a certain pH), and to permit the oxidation to occur. A suitable pH may be effected by choosing acidic (pH<7), alkaline (pH>7), or neutral (pH=7) oxidizers, sequentially or combined with other chemical components, in general acids or bases, that affect the pH. The methods of determining the pH of a chemical compound or a mixture of chemical compounds, and adjusting the pH are well known to those skilled in the art.

Example 1: Preferred compositions are comprised of an alkaline compound in combination with an oxidizer, in an aqueous solution, for example:

- A) 0.1 10% of sodium hydroxide and 0.1 35% of hydrogen peroxide by weight in water; or
- B) 0.1 20% of sodium carbonate and 0.1 20% of sodium percarbonate by weight in water; or
- C) 0.1 20% of sodium carbonate and 0.1 35% of hydrogen peroxide by weight in water.

Example 2: Preferred compositions are comprised of an alkaline oxidizer, in an aqueous solution, for example:

- D) 0.1 10% of sodium peroxide by weight in water; or
- E) 0.1 20% of sodium percarbonate by weight in water.

- Example 3: Preferred compositions are comprised of a neutral oxidizer in an aqueous solution, for example:
- F) 0.1 35% of hydrogen peroxide by weight in water.
- Example 4: Preferred compositions are comprised of an acidic compound in combination with an oxidizer, in an aqueous solution, for example:
- G) 0.1 10% of hydrogen chloride and 0.1 35% of hydrogen peroxide by weight in water.
- Example 5: Preferred compositions are comprised of an acidic oxidizer, in an aqueous solution, for example:
- H) 0.1 10% of ammonium persulfate by weight in water.
- The application may take place either indoors or outdoors. To treat a substrate, a metal compound is applied to the substrate according to known methods. Oxidative conditions may be assured by selection of a suitable oxidizer, and may require the use of additional acids or bases before, during, or after the application of the metal compound or the oxidizer. After the metal compound is applied to the substrate, the applicator contacts the substrate with an oxidizer to increase the development speed of the color. This is typically accomplished by brushing, rolling, spraying, sponging, squeegeeing, sweeping, sprinkling, or otherwise applying the oxidizer onto the substrate and allowing it to react. Sprinkling may be carried out by sprinkling the oxidizer as a powder onto the substrate and then spraying the powder-covered substrate with an aqueous mist. The oxidizer may be applied undiluted or diluted in a liquid solvent in amounts from 0.1% to 100% by weight. Liquid solvents include water, or organic solvents, such as toluene and xylene, or mixtures of solvents.

- Minutes, for example 5 to 15 minutes, after application of the oxidizer, work may be commenced to finish the staining process, for example the substrate may then be rinsed and further protected and finished according to conventional practices. By this method, the development speed of the color may be increased from hours to minutes, resulting in a two-fold, four-fold, ten-fold or greater increase in the development speed.
- As a specific example, a concrete substrate is treated with a solution of manganese(II)chloride and iron(II)chloride in water, according to known methods. At the pH of concrete, and even after raising the pH with a base such as sodium hydroxide, development of the brown color, originating from the formation of manganese(IV) and iron(III) cations, is very slow and may take hours to occur. After the application of an oxidizer, such as 4% hydrogen peroxide (by weight) and 1% sodium hydroxide (by weight) in water, color development is completed within less than 5 minutes compared with more than 24 hours in conventional conditions. Safety considerations may dictate an upper limit on the concentration of the oxidizer, for example 35% or 50% by weight for hydrogen peroxide in aqueous solution.
- 19 Typical reactions that occur are:
- (a)  $2MnCl_2 + O_2 + 2Ca(OH)_2$   $\longrightarrow$   $2MnO(OH)_2 + 2CaCl_2$  (very slow reaction)

Equation (a) shows a reaction of a metal compound under alkaline (concrete) and atmospheric conditions. The reaction remains slow even if the pH is raised with alkali.

(b) 
$$MnCl_2 + 2NaOH$$
  $\longrightarrow$   $Mn(OH)_2 + 2NaCl$  (fast reaction)

(c) 
$$Mn(OH)_2 + H_2O_2$$
  $\longrightarrow$   $MnO(OH)_2 + H_2O$  (fast reaction)

Equations (b) and (c) show a reaction of a metal compound under alkaline conditions, and the subsequent oxidation of the reaction product with an oxidizer.

(d) 
$$2\text{FeCl}_2 + \text{H}_2\text{O}_2 + 2\text{Ca}(\text{OH})_2$$
  $\longrightarrow$   $2\text{FeO}(\text{OH}) + 2\text{H}_2\text{O} + 2\text{CaCl}_2$  (fast reaction)

Equation (d) shows a reaction of a metal compound under alkaline conditions in presence of an oxidizer.

Immaterial modifications may be made to the invention described here without departing from the essence of the invention.